Structural Investigation of Solid Solutions in the System $USiO_4$ – $ThSiO_4$

S. Labs[1], S. Weiss[2], C. Hennig[2], H. Curtius[1], D. Bosbach[1].

[1]Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research - IEK-6, D-52428 Jülich, Germany.
[2]Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Bautzner Landstraße 400, D-01314 Dresden.

Introduction

- Coffinite, $USiO_4$, is the second most important uranium ore.
- Under reducing conditions with water and high silica concentrations ($c(SiO_4) \geqq 10^{-4}$ mol/L) the reaction of UO_2 to $USiO_4$ is favoured (**Langmuir's criterion**)[1].
- Coffinite therefore is a potential secondary phase in a deep geological repository for spent nuclear fuel.
- Estimates on the solubility of $USiO_4$ indicate a significantly lower U-solubility compared to that of UO_2.[2,3]

  ⟶ Significant **reduction of U-source term**!
- Reliable and **valdidated thermodynamic data** are **missing**.
- Use of **natural samples is not feasible** due to major amounts of impurities.
- Synthesis of $USiO_4$ challenging[3,4,5] **–** $ThSiO_4$ easily achievable.
- Implications from $U_xTh_{(1-x)}SiO_4$ for pure $USiO_4$.

Figure 1. Natural coffinite sample

Synthesis

All experimental procedures were carried out under protective atmosphere in a glove box (N_2, O_2 < 10 ppm). $U_xTh_{(1-x)}SiO_4$ were synthesized by adding UCl_4 and $ThCl_4$ stock solutions in stoichiometric amounts to an excess amount of Na_2SiO_3 solution and adjusting the pH to ~ 8. The greenish precipitate is centrifuged and mixed with a $NaHCO_3$ buffer. This slurry is hydrothermally treated at 250 °C, then very slowly cooled down. The obtained product is washed with distilled water and dried.

Analytical Equipment

X- ray diffraction *D8* by *Bruker AXS GmbH* using Cu Kα, *VÅrnTec* detector, ($\Delta 2\theta$ = 0.021, 2θ = 15 - 130°, t = 10 s/step).
EXAFS were measured at the *Rossendorf beamline*, BM-20 (ESRF) employing the UL_3 - edge at 17185 eV and ThL_3 - edge at 16310 eV.

Results

X-ray diffraction

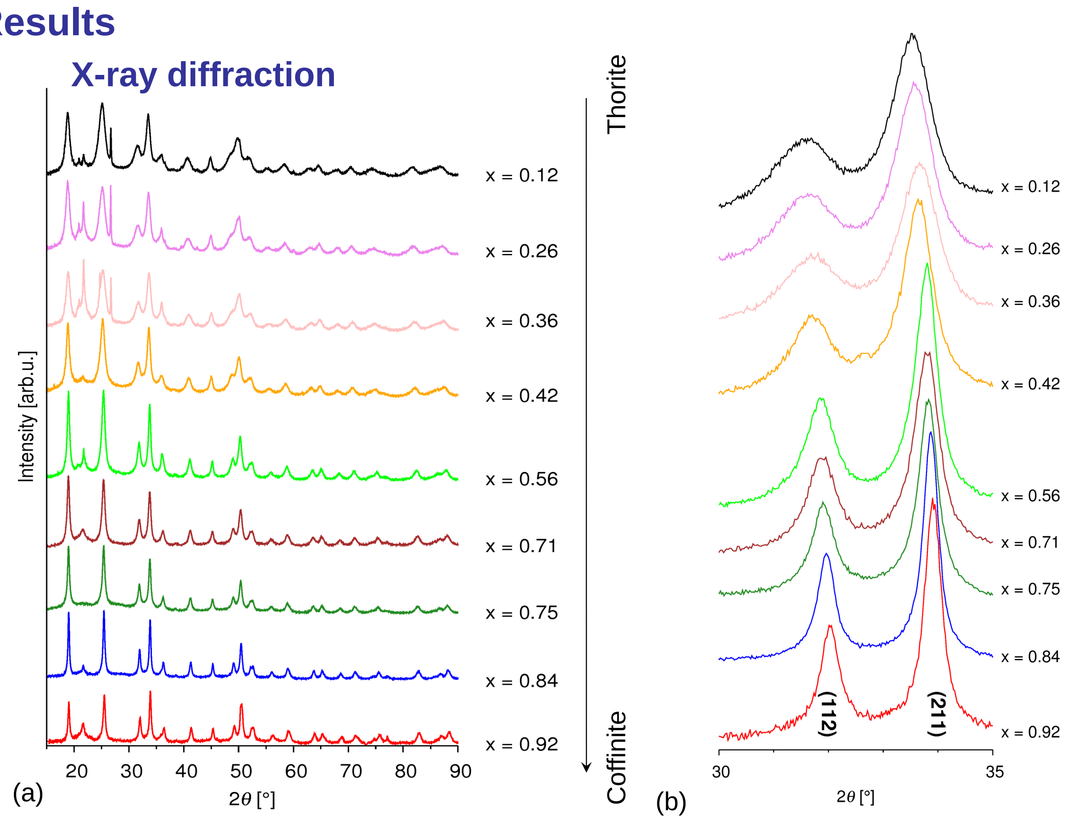

Figure 2. (a) Diffraction pattern of the solid solutions with mole fraction, x = 0.12 – 0.92. (b) Close up of the 30 – 35° 2θ region.

- All synthesized products exhibit the typical pattern for spacegroup $I\,4_1/amd$.
- Glassy silica visible around 21° 2θ, below x = 0.4 also α-SiO_2 (strong reflection at ~ 26° 2θ,
- Reflections shift to higher 2θ with decreasing x, broadening becomes evident.

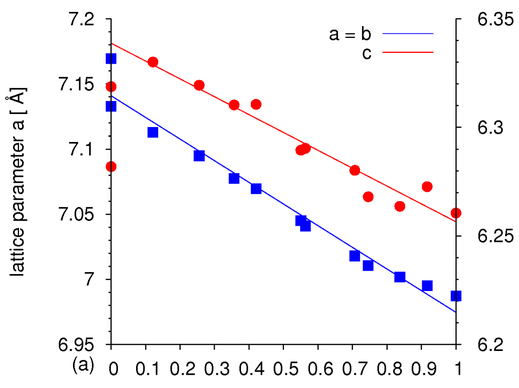

Figure 5. Lattice parameters c and a = b dependence on x and linear fit.

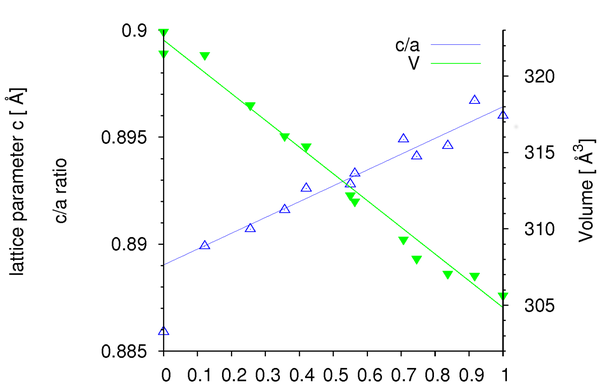

Figure 6. Cell volume and c/a-ratio dependence on x with linear fit.

- Unit cell of $USiO_4$ smaller than for $ThSiO_4$.
- Values of c, a=b, V steadily decrease with increasing x and establish Vegard like behavior.

EXAFS

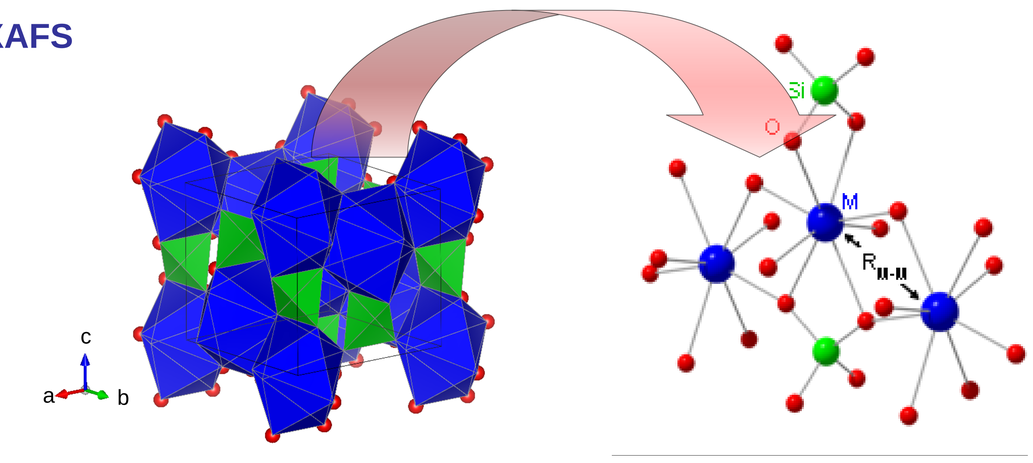

Figure 3. Unit cell of $MSiO_4$ with coordination polyhedra (Blue = U/Th, green = Si, red = O - atoms). [M(IV)O_8] polyhedra form alternating chains connected by the isolated [SiO_4] tetrahedra.

Figure 4. Illustration of the local environment in the zircon-type structure. $R_{M\text{-}M}$ represents the three possible metal – metal distances $R_{Th\text{-}Th}$ and $R_{Th\text{-}U}$ and $R_{U\text{-}U}$.

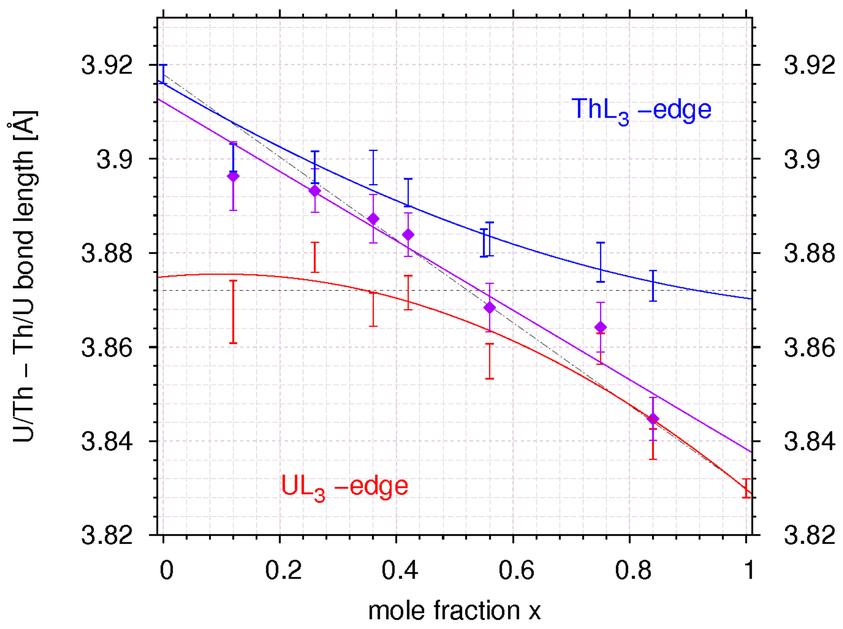

Figure 7. Distances $R_{M\text{-}M}$ of UL_3- (red) and ThL_3-edge (blue) with gaussian fits, weighed averages and linear fit (purple). The dashed line refers to the virtual crystal approximation (VCA), the dotted line represents the average distance of the end members.

- No discontinuities visible ⟶ no miscibility gap evident.
- Weighed average distances close to Vegard line.
- Conformance of short range order and long range order.

Conclusion

- Solid solutions of $U_xTh_{(1-x)}SiO_4$ were synthesized in the range x = 0.1 – 0.95
- No presence of the oxide, $U_yTh_{(1-y)}O_2$.
- XRD data show accordance to Vegard's Law ⟶ complete miscibility!
- Significant broadening effect of the reflections in the Th-rich members.
- EXAFS data confirms full solid solution series.
- No indication for clustering or segregation.

⟶ **Complete solid solution established!**

Outlook

- High pressure-synchrotron diffraction and high pressure-Raman investigation ongoing.
- High Resolution Powder Diffraction study of $U_xTh_{(1-x)}SiO_4$ solid solutions ongoing.

  ⟶ Determination of oxygen positions.
- Washing procedure (removal of excess silica).
- Calorimetric measurements in preparation.

References
[1] D. Langmuir, Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits, *Geochim. Cosmochim. Acta* (1978) 42, 547-569, [2] Hemingway, B. S.; Thermodynamic properties of selected uranium compounds and aqueous species at 298.15 K and 1 bar and at higher temperatures. Preliminary models for the origine of coffinite deposits. *US Geological Survey* (1982) 89. [3] Szenknect, S. et al.; From Uranothorites to Coffinite: A Solid Solution Route to the Thermodynamic Properties of $USiO_4$. *Inorg. Chem.* (2013) 52 (12), 6957–6968. [4] V. Pointeau et al. Synthesis and characterization of coffinite, *J. Nuc. Mat.* (2009) 393, 449-458 [5] D. Costin et al., How to explain the difficulties in the coffinite synthesis from the study of uranothorite?, *Inorg. Chem.* (2011) 50 (21) ,11117-111126.

Acknowledgment

We gratefully acknowledge that beamtime at the Rossendorf beamline (ESRF) was granted through ACTINET-i3, proposal No.: AC4-JRP04 . Financial support was provided through German Federal Ministry of Education and Research (BMBF), ImmoRad Project (Grant No. 02NUK019C) .

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